

19 Federal Republic  
of Germany



German  
Patent Office

12 **Offenlegungsschrift**  
[Unexamined Patent Application]

10 **DE 43 32 009 A1**

21 Application Number: P 43 32 009.0  
22 Filing Date: 21 September 1993  
43 Date of Publication of the  
Unexamined Patent Application: 30 March 1995

51 Int. Cl.<sup>6</sup>  
C 07 F 17/00  
C 07 F 7/00  
// C 07 F 7/22  
7/02  
7/28  
C 08 F 4/642  
4/68

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The following text is taken from the documents submitted by the applicant.

54 Method for producing organometallic fluorides

57  $\pi$ -system-containing organometallic fluorides are obtained by reacting a fluorine-free organometallic halide with a tin fluoride with the general formula  $R^4_3SnF$  wherein the groups  $R^4$  are the same or different and represent  $C_1$  to  $C_{10}$  alkyl,  $C_6$  to  $C_{14}$  aryl,  $C_2$  to  $C_{10}$  alkenyl,  $C_7$  to  $C_{20}$  arylalkyl, or  $C_7$  to  $C_{15}$  alkylaryl.

### Description

This invention relates to a method for producing  $\pi$ -system-containing organometallic fluorides that can be advantageously used as catalysts or catalyst components, in particular for polyolefin production.

Cyclopentadienyltitanium, -zirconium, and -hafnium complexes are used in combination with aluminoxane as catalysts for producing polyolefins. The corresponding di- and trichloride derivatives are particularly important as highly active olefin polymerization catalysts (*Adv. in Organomet. Chem.*, Vol. 18 (1988), pp. 99-149). Unbridged zirconocene difluorides are also known (*J. Chem. Soc. (A)* (1971), pp. 2225-2229; *J. Chem. Soc. Dalton Trans.* (1987), pp. 1463-1472).

It is known that the corresponding organometallic fluorides can be produced from transition metal chlorides and arsenic trifluoride by metathesis (*J. Chem. Soc. Dalton Trans.* (1990), p. 713). However, the reaction of pentamethylcyclopentadienylzirconium trichloride (or pentamethylcyclopentadienylhafnium trichloride) with arsenic trifluoride gives pentamethylcyclopentadienylarsenic dichloride in high yields. In addition to fluorine-to-chlorine exchange, the cyclopentadienyl ring is also transferred to the arsenic atom. Moreover, it is frequently quite difficult to separate excess arsenic trifluoride from the reaction product.

Therefore, the object was to find a method for producing  $\pi$ -system-containing organometallic fluorides that avoids the known disadvantages of the prior art.

Surprisingly, it was found that  $\pi$ -system-containing organometallic fluorides can be very easily synthesized on a preparative scale in very good yields using tin fluoride. To this end, a mixture of a tin fluoride and a fluorine-free organometallic halide is reacted in a solvent; this reaction can be run in technically favorable solvents such as aliphatic and aromatic hydrocarbons. The organometallic fluoride can be directly isolated after removal of all the volatile components. In addition, the tin fluoride can be easily recovered from the tin chloride product and reused as fluorinating agent.

This exchange of chlorine, bromine, or iodine with fluorine allows gradations in reactivity, primarily for influencing catalyst properties, to be obtained.

The invention relates to a method for producing  $\pi$ -system-containing organometallic fluorides with general formulas I, II, III, IV, V, and VI



wherein

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

the groups  $\text{R}^1$  are the same or different and represent hydrogen,  $\text{C}_1$  to  $\text{C}_{20}$  alkyl,  $\text{C}_6$  to  $\text{C}_{14}$  aryl,  $\text{C}_2$  to  $\text{C}_{10}$  alkenyl,  $\text{C}_7$  to  $\text{C}_{20}$  arylalkyl, or  $\text{C}_7$  to  $\text{C}_{15}$  alkylaryl, or  $\text{SiR}^3_3$  (wherein  $\text{R}^3$  is  $\text{C}_1$  to  $\text{C}_{10}$  alkyl), or neighboring  $\text{R}^1$  groups form one or several aliphatic or aromatic ring systems with the atoms that connect said  $\text{R}^1$  groups,

the groups  $\text{R}^5$  are the same or different and represent  $\text{C}_1$  to  $\text{C}_{10}$  alkyl,  $\text{C}_6$  to  $\text{C}_{10}$  aryl,  $\text{C}_1$  to  $\text{C}_{10}$  alkylaryl,  $\text{NR}^6_2$ ,  $\text{OR}^6$ ,  $\text{SR}^6$ ,  $\text{OSiR}^6_3$ ,  $>\text{NR}^6$ ,  $\text{PR}^6_2$ , or  $>\text{PR}^6$ , wherein each  $\text{R}^6$  is independently selected from hydrogen,  $\text{C}_1$  to  $\text{C}_{10}$  alkyl, and  $\text{C}_6$  to  $\text{C}_{10}$  aryl, and

$p = 1, 2, \text{ or } 3$ ,  $o = 0, 1, \text{ or } 2$ ,  $m = 4 - (p + o)$ ,  $n = 1, 2, 3, 4, \text{ or } 5$ ,  $(p + o) = 1, 2, \text{ or } 3$ ,  $q = 2$  when  $m = 1$ ,  $p = 1$ , and  $\text{R}^5 = >\text{NR}^6$  or  $>\text{PR}^6$ , and otherwise  $q = 1$ ;



wherein

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

the groups  $\text{R}^1$  are the same or different and represent hydrogen,  $\text{C}_1$  to  $\text{C}_{20}$  alkyl,  $\text{C}_6$  to  $\text{C}_{14}$  aryl,  $\text{C}_2$  to  $\text{C}_{10}$  alkenyl,  $\text{C}_7$  to  $\text{C}_{20}$  arylalkyl, or  $\text{C}_7$  to  $\text{C}_{15}$  alkylaryl, or  $\text{SiR}^3_3$  (wherein  $\text{R}^3$  is  $\text{C}_1$  to  $\text{C}_{10}$  alkyl), or neighboring  $\text{R}^1$  groups form one or several aliphatic or aromatic ring systems with the atoms that connect said  $\text{R}^1$  groups,

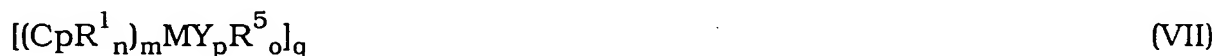
the groups  $\text{R}^2$  are the same or different and represent hydrogen,  $\text{C}_1$  to  $\text{C}_{20}$  alkyl,  $\text{C}_6$  to  $\text{C}_{14}$  aryl,  $\text{C}_2$  to  $\text{C}_{10}$  alkenyl,  $\text{C}_7$  to  $\text{C}_{20}$  arylalkyl, or  $\text{C}_7$  to  $\text{C}_{15}$

alkylaryl, or neighboring  $R^2$  groups form a ring system with the atoms that connect said  $R^2$  groups,  
the groups  $R^5$  are the same or different and represent  $C_1$  to  $C_{10}$  alkyl,  $C_6$  to  $C_{10}$  aryl,  $C_1$  to  $C_{10}$  alkylaryl,  $NR^6$ ,  $OR^6$ ,  $SR^6$ ,  $OSiR^6_3$ ,  $>NR^6$ ,  $PR^6_2$ , or  $>PR^6$ , wherein each  $R^6$  is independently selected from hydrogen,  $C_1$  to  $C_{10}$  alkyl, and  $C_6$  to  $C_{10}$  aryl,  
B is carbon or silicon, and  
**k** = 1, 2, or 3, **p** = 1 or 2, **o** = 0 or 1, **n** = 1, 2, 3, 4, or 5, (**p** + **o**) = 2, **q** = 2 when **m** = 1, **p** = 1, and  $R^5 = >NR^6$  or  $>PR^6$ , and otherwise **q** = 1;



wherein Cp,  $R^1$ ,  $R^2$ , M, B, **k**, and **n** are defined as in formula II,

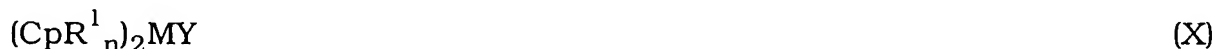
said method being characterized by reacting a compound with general formula VII, VIII, IX, X, XI, or XII



wherein Cp,  $R^1$ ,  $R^5$ ,  $R^6$ , M, **p**, **o**, **m**, **n**, and **q** are defined as in formula I and Y is chlorine, bromine, or iodine



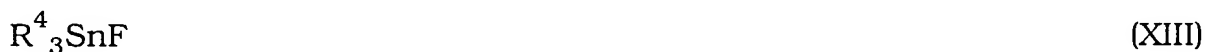
wherein Cp,  $R^1$ ,  $R^2$ ,  $R^5$ ,  $R^6$ , M, B, **k**, **p**, **o**, **n**, and **q** are defined as in formula II and Y is chlorine, bromine, or iodine





wherein Cp,  $R^1$ ,  $R^2$ , B, Y, **k**, and **n** are defined as in formula II

in an inert solvent with a tin fluoride with general formula XIII



wherein the groups  $R^4$  are the same or different and represent  $C_1$  to  $C_{10}$  alkyl,  $C_6$  to  $C_{14}$  aryl,  $C_2$  to  $C_{10}$  alkenyl,  $C_7$  to  $C_{20}$  arylalkyl, or  $C_7$  to  $C_{15}$  alkylaryl.

In preferred embodiments of formulas I through XII, M is titanium, zirconium, or hafnium; the groups  $R^1$  are the same or different and represent hydrogen,  $C_1$  to  $C_4$  alkyl,  $C_6$  to  $C_{12}$  aryl,  $C_2$  to  $C_6$  alkenyl,  $C_7$  to  $C_{15}$  arylalkyl,  $C_7$  to  $C_{15}$  alkylaryl, or  $SiR^3_3$  (wherein  $R^3$  is  $C_1$  to  $C_4$  alkyl) or neighboring  $R^1$  groups form an aliphatic or aromatic ring system; the groups  $R^2$  are the same or different and represent hydrogen,  $C_1$  to  $C_4$  alkyl,  $C_6$  to  $C_{12}$  aryl,  $C_2$  to  $C_6$  alkenyl,  $C_7$  to  $C_{15}$  arylalkyl, or  $C_7$  to  $C_{15}$  alkylaryl; the groups  $R^5$  are the same or different and represent  $C_1$  to  $C_{10}$  alkyl or  $>NR^6$ ; and **k** = 1 or 2, **p** = 2 or 3, **o** = 0, and **q** = 1; and Y in formulas VII through XII is preferably chlorine.

In particularly preferred embodiments, M is zirconium or titanium;  $R^1$  is hydrogen,  $C_1$  to  $C_4$  alkyl,  $C_6$  to  $C_{10}$  aryl, or  $SiR^3_3$  wherein  $R^3$  is  $C_1$  to  $C_4$  alkyl, or neighboring  $R^1$  groups form a substituted or unsubstituted, aliphatic or aromatic six-membered ring;  $R^2$  is  $C_1$  to  $C_4$  alkyl or phenyl; **k** = 1 when B is silicon and **k** = 2 when B is carbon; **p** = 2; **o** = 0; and **q** = 1.

$R^4$  in formula XIII is preferably  $C_1$  to  $C_4$  alkyl and particularly methyl.

In all formulas, "alkyl" denotes linear or branched alkyl.

The reaction of a compound with formula VII or VIII to give a compound with formula I or II is preferred. Titanium, zirconium, and hafnium can occur in formulas I through XII in an oxidation state of +3 or +4.

The following examples serve to illustrate the organometallic fluorides described in general formulas I through VI in more detail, but are not to be construed as all inclusive.

ethylenebis(indenyl)zirconium difluoride  
ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium difluoride  
ethylenebis(2-methylindenyl)zirconium difluoride  
ethylenebis(2,4-dimethylindenyl)zirconium difluoride  
dimethylsilandiylbis(2-methyl-4,5-benzoindenyl)zirconium difluoride  
dimethylsilandiylbis(2-methyl-4,6-diisopropylindenyl)zirconium difluoride  
dimethylsilandiylbis(2-methyl-4-phenylindenyl)zirconium difluoride  
dimethylsilandiylbis(2-ethyl-4-phenylindenyl)zirconium difluoride  
dimethylsilandiylbis(2-methyl-4-(1-naphthyl)indenyl)zirconium difluoride  
dimethylsilandiylbis(indenyl)zirconium difluoride  
dimethylsilandiylbis(2-methyl-4-ethylindenyl)zirconium difluoride  
dimethylsilandiylbis(2-methyl-4-isopropylindenyl)zirconium difluoride  
dimethylsilandiylbis(2-methyl-4-methylindenyl)zirconium difluoride  
dimethylsilandiylbis(2-ethyl-4-methylindenyl)zirconium difluoride  
dimethylsilandiylbis(2-methyl- $\alpha$ -acenaphth-1-indenyl)zirconium difluoride  
phenylmethylsilandiylbis(2-methyl-4-phenylindenyl)zirconium difluoride  
phenylmethylsilandiylbis(2-methylindenyl)zirconium difluoride  
ethylenebis(2-methyl-4,5-benzoindenyl)zirconium difluoride  
ethylenebis(2-methyl-4,6-diisopropylindenyl)zirconium difluoride  
ethylenebis(2-methyl-4-phenylindenyl)zirconium difluoride  
ethylenebis(2-ethyl-4-phenylindenyl)zirconium difluoride  
ethylenebis(2-methyl-4-(1-naphthyl)indenyl)zirconium difluoride  
ethylenebis(indenyl)zirconium difluoride  
ethylenebis(2-methyl-4-ethylindenyl)zirconium difluoride  
ethylenebis(2-methyl-4-isopropylindenyl)zirconium difluoride  
ethylenebis(2-methyl-4-methylindenyl)zirconium difluoride  
ethylenebis(2-ethyl-4-methylindenyl)zirconium difluoride  
ethylenebis(2-methyl- $\alpha$ -acenaphth-1-indenyl)zirconium difluoride  
bis(2-methyl-4,5-benzoindenyl)zirconium difluoride  
bis(2-methyl-4,6-diisopropylindenyl)zirconium difluoride  
bis(2-methyl-4-phenylindenyl)zirconium difluoride

bis(2-ethyl-4-phenylindenyl)zirconium difluoride  
 bis(2-methyl-4-(1-naphthyl)indenyl)zirconium difluoride  
 bis(indenyl)zirconium difluoride  
 bis(2-methyl-4-ethylindenyl)zirconium difluoride  
 bis(2-methyl-4-isopropylindenyl)zirconium difluoride  
 bis(2-methyl-4-methylindenyl)zirconium difluoride  
 bis(2-ethyl-4-methylindenyl)zirconium difluoride  
 bis(2-methyl- $\alpha$ -acenaphth-1-indenyl)zirconium difluoride  
 bis(*n*-butylcyclopentadienyl)zirconium difluoride  
 bis(cyclopentadienyl)zirconium difluoride  
 bis(pentamethylcyclopentadienyl)zirconium difluoride  
 cyclopentadienylzirconium trifluoride  
 pentamethylcyclopentadienylzirconium trifluoride  
 (2-methyl-4,5-benzoidenyl)zirconium trifluoride  
 (2-methyl-4,6-diisopropylindenyl)zirconium trifluoride  
 (2-methyl-4-phenylindenyl)zirconium trifluoride  
 (2-ethyl-4-phenylindenyl)zirconium trifluoride  
 (2-methyl-4-(1-naphthyl)indenyl)zirconium trifluoride  
 indenylzirconium trifluoride  
 (2-methyl-4-ethylindenyl)zirconium trifluoride  
 (2-methyl-4-isopropylindenyl)zirconium trifluoride  
 (2-methyl-4-methylindenyl)zirconium trifluoride  
 (2-ethyl-4-methylindenyl)zirconium trifluoride  
 (2-methyl- $\alpha$ -acenaphth-1-indenyl)zirconium trifluoride  
 (*n*-butylcyclopentadienyl)zirconium trifluoride  
 isopropylidene(9-fluorenyl)cyclopentadienylzirconium difluoride  
 diphenylmethylen(9-fluorenyl)cyclopentadienylzirconium difluoride  
 phenylmethylen(9-fluorenyl)cyclopentadienylzirconium difluoride  
 dimethylsilandiyl(9-fluorenyl)cyclopentadienylzirconium difluoride  
 isopropylidene(9-fluorenyl)(3-methylcyclopentadienyl)zirconium difluoride  
 diphenylmethylen(9-fluorenyl)(3-methylcyclopentadienyl)zirconium difluoride  
 phenylmethylen(9-fluorenyl)(3-methylcyclopentadienyl)zirconium difluoride  
 dimethylsilandiyl(9-fluorenyl)(3-methylcyclopentadienyl)zirconium difluoride  
 isopropylidene(9-fluorenyl)(3-isopropylcyclopentadienyl)zirconium difluoride  
 diphenylmethylen(9-fluorenyl)(3-isopropylcyclopentadienyl)zirconium difluoride  
 phenylmethylen(9-fluorenyl)(3-isopropylcyclopentadienyl)zirconium difluoride

dimethylsilandiyl(9-fluorenyl)(3-isopropylcyclopentadienyl)zirconium difluoride  
 isopropylidene(2,7-di-*tert*-butyl-9-fluorenyl)cyclopentadienylzirconium difluoride  
 diphenylmethylene(2,7-di-*tert*-butyl-9-fluorenyl)cyclopentadienylzirconium difluoride  
 phenylmethylmethylene(2,7-di-*tert*-butyl-9-fluorenyl)cyclopentadienylzirconium  
 difluoride  
 dimethylsilandiyl(2,7-di-*tert*-butyl-9-fluorenyl)cyclopentadienylzirconium difluoride  
 ethylenebis(indenyl)titanium difluoride  
 ethylenebis(4,5,6,7-tetrahydroindenyl)titanium difluoride  
 ethylenebis(2-methylindenyl)titanium difluoride  
 dimethylsilandiylbis(indenyl)titanium difluoride  
 bis(indenyl)titanium difluoride  
 bis(cyclopentadienyl)titanium difluoride  
 bis(pentamethylcyclopentadienyl)titanium difluoride  
 cyclopentadienyltitanium trifluoride  
 pentamethylcyclopentadienyltitanium trifluoride  
 indenyltitanium trifluoride  
 (*n*-butylcyclopentadienyl)titanium trifluoride  
 isopropylidene(9-fluorenyl)cyclopentadienyltitanium difluoride  
 ethylenebis(indenyl)hafnium difluoride  
 ethylenebis(4,5,6,7-tetrahydroindenyl)hafnium difluoride  
 ethylenebis(2-methylindenyl)hafnium difluoride  
 dimethylsilandiylbis(indenyl)hafnium difluoride  
 bis(indenyl)hafnium difluoride  
 bis(cyclopentadienyl)hafnium difluoride  
 bis(pentamethylcyclopentadienyl)hafnium difluoride  
 cyclopentadienylhafnium trifluoride  
 pentamethylcyclopentadienylhafnium trifluoride  
 indenylhafnium trifluoride  
 (*n*-butylcyclopentadienyl)hafnium trifluoride  
 isopropylidene(9-fluorenyl)cyclopentadienylhafnium difluoride  
 bis(cyclopentadienyl)titanium fluoride  
 bis(methylcyclopentadienyl)titanium fluoride  
 bis(pentamethylcyclopentadienyl)titanium fluoride  
 $[(\text{Me}_3\text{SiC}_5\text{H}_4)\text{Ti}(\text{F})\text{Nt-Bu}]_2$



The organometallic halides required as starting compounds are commercially available, or can be produced by methods known from the literature. The tin fluorides with formula XIII required as starting materials can be produced by methods known from the literature (*Ber. Dtsch. Chem. Ges.* (1918), Vol. 51, p. 1447).

The reaction is carried out in an inert solvent such as hexane, toluene, or methylcyclohexane, preferably in toluene.

The reaction can be run at temperatures ranging from -50 to 120°C, preferably 25 to 100°C.

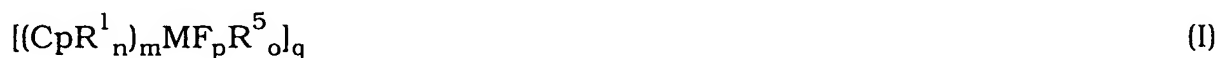
The molar ratio of the reactants is determined by the number of halogen atoms to be substituted in the organometallic compound. While an excess of tin fluoride with formula XIII can be used, the tin fluoride with formula XIII is preferably used in stoichiometric quantities.

After the reaction is completed, the volatile components are removed and the solvent reused. The tin fluoride with formula XIII may be recovered from the resulting tin halide (*Ber. Dtsch. Chem. Ges.* (1918), Vol. 51, p. 1447).

The organometallic fluorides with formulas I, II, III, IV, V, and VI are obtained in very good yields, preferably greater than 85%. Further purification can generally be omitted.

The inventive method for producing organometallic fluorides is characterized in that it is technically simple to perform and requires commonly available starting materials. The solvent can be reused and the fluorinating agent can be recovered.

Moreover, the method according to the invention enables the production of certain  $\pi$ -system-containing organometallic fluorides not available using previous methods. The present invention thus applies to the following compounds with formulas I, II, III, IV, V, and VI



in which

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

the groups  $R^1$  are the same or different and represent hydrogen,  $C_1$  to  $C_{20}$  alkyl,  $C_6$  to  $C_{14}$  aryl,  $C_2$  to  $C_{10}$  alkenyl,  $C_7$  to  $C_{20}$  arylalkyl, or  $C_7$  to  $C_{15}$  alkylaryl, or  $SiR^3_3$  (wherein  $R^3$  is  $C_1$  to  $C_{10}$  alkyl) or neighboring  $R^1$  groups form one or several aliphatic or aromatic ring systems with the atoms that join said  $R^1$  groups,

the groups  $R^5$  are the same or different and represent  $C_1$  to  $C_{10}$  alkyl,  $C_6$  to  $C_{10}$  aryl,  $C_1$  to  $C_{10}$  alkylaryl,  $NR^6_2$ ,  $OR^6$ ,  $SR^6$ ,  $OSiR^6_3$ ,  $NR^6$ ,  $PR^6_2$ , or  $PR^6$  (wherein the groups  $R^6$  are the same or different and represent hydrogen,  $C_1$  to  $C_{10}$  alkyl, or  $C_6$  to  $C_{10}$  aryl), and

$p = 1$  or  $3$ ,  $o = 0, 1$ , or  $2$ ,  $m = 4 - (p + o)$ ,  $n = 1, 2, 3, 4$ , or  $5$ ,  $(p + o) = 1, 2$ , or  $3$ ,  $q = 2$  when  $m = 1$ ,  $p = 1$ , and  $R^5 = >NR^6$  or  $>PR^6$ , and otherwise  $q = 1$ ;



in which

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

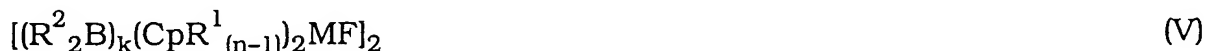
the groups  $R^1$  are the same or different and represent hydrogen,  $C_1$  to  $C_{20}$  alkyl,  $C_6$  to  $C_{14}$  aryl,  $C_2$  to  $C_{10}$  alkenyl,  $C_7$  to  $C_{20}$  arylalkyl, or  $C_7$  to  $C_{15}$  alkylaryl, or  $SiR^3_3$  (wherein  $R^3$  is  $C_1$  to  $C_{10}$  alkyl), or neighboring  $R^1$  groups form one or several aliphatic or aromatic ring systems with the atoms that join said  $R^1$  groups,

the groups  $R^2$  are the same or different and represent hydrogen,  $C_1$  to  $C_{20}$  alkyl,  $C_6$  to  $C_{14}$  aryl,  $C_2$  to  $C_{10}$  alkenyl,  $C_7$  to  $C_{20}$  arylalkyl, or  $C_7$  to  $C_{15}$  alkylaryl, or neighboring  $R^2$  groups form a ring system with the atoms that join said  $R^2$  groups,

the groups  $R^5$  are the same or different and represent  $C_1$  to  $C_{10}$  alkyl,  $C_6$  to  $C_{10}$  aryl,  $C_1$  to  $C_{10}$  alkylaryl,  $NR^6_2$ ,  $OR^6$ ,  $SR^6$ ,  $OSiR^6_3$ ,  $>NR^6$ ,  $PR^6_2$ , or  $>PR^6$ , (wherein the groups  $R^6$  are the same or different and represent hydrogen,  $C_1$  to  $C_{10}$  alkyl, or  $C_6$  to  $C_{10}$  aryl),

B is carbon or silicon, and

$k = 1, 2$ , or  $3$ ,  $p = 1$  or  $2$ ,  $o = 0$  or  $1$ ,  $n = 1, 2, 3, 4$ , or  $5$ ,  $(p + ) = 2$ ,  $q = 2$  when  $m = 1$ ,  $p = 1$ , and  $R^5 = >NR^6$  or  $>PR^6$ , and otherwise  $q = 1$ ;



in which Cp,  $\text{R}^1$ ,  $\text{R}^2$ , M, B, **k**, and **n** are defined as in formula II.

In preferred embodiments of formulas I through VI,

M is titanium, zirconium, or hafnium,

the groups  $\text{R}^1$  are the same or different and represent hydrogen,  $\text{C}_1$  to  $\text{C}_4$  alkyl,  $\text{C}_6$  to  $\text{C}_{12}$  aryl,  $\text{C}_2$  to  $\text{C}_6$  alkenyl,  $\text{C}_7$  to  $\text{C}_{15}$  arylalkyl,  $\text{C}_7$  to  $\text{C}_{15}$  alkylaryl, or  $\text{SiR}^3_3$  (wherein  $\text{R}^3$  is  $\text{C}_1$  to  $\text{C}_4$  alkyl), or neighboring  $\text{R}^1$  groups form an aliphatic or aromatic ring system,

the groups  $\text{R}^2$  are the same or different and represent hydrogen,  $\text{C}_1$  to  $\text{C}_4$  alkyl,

$\text{C}_6$  to  $\text{C}_{12}$  aryl,  $\text{C}_2$  to  $\text{C}_6$  alkenyl,  $\text{C}_7$  to  $\text{C}_{15}$  arylalkyl, or  $\text{C}_7$  to  $\text{C}_{15}$  alkylaryl, the groups  $\text{R}^5$  are the same or different and represent  $\text{C}_1$  to  $\text{C}_{10}$  alkyl or  $>\text{NR}^6$ ,

B is carbon or silicon, and

**k** = 1 or 2 and **q** = 1.

In formula II, **p** is preferably 2, **o** = 0, and **q** = 1.

In particularly preferred embodiments, M is zirconium or titanium;  $\text{R}^1$  is hydrogen,  $\text{C}_1$  to  $\text{C}_4$  alkyl,  $\text{C}_6$  to  $\text{C}_{12}$  aryl, or  $\text{SiR}^3_3$  (wherein  $\text{R}^3$  is  $\text{C}_1$  to  $\text{C}_4$  alkyl), or neighboring  $\text{R}^1$  groups form a substituted or unsubstituted, aliphatic or aromatic six-membered ring;  $\text{R}^2$  is  $\text{C}_1$  to  $\text{C}_4$  alkyl or phenyl; **k** = 1 when B is silicon; **k** = 2 when B is carbon; and **q** = 1.

The  $\pi$ -system-containing organometallic fluorides according to the invention are very thermally stable and are therefore particularly suitable for catalysts that are used at high temperatures.

The following examples explain the invention in additional detail.

## Examples

### Example A

#### Pentamethylcyclopentadienylzirconium trifluoride

A mixture of 5.0 g (15.0 mmol) pentamethylcyclopentadienylzirconium trichloride and 8.2 g (45.1 mmol)  $\text{Me}_3\text{SnF}$  was combined with 80 mL toluene and stirred at room temperature. A slightly turbid solution formed after 0.5 hr. The mixture was heated at the boiling point for 0.1 hr to complete the reaction. The mixture was allowed to cool and undissolved impurities were filtered off. The colorless solid remaining after evaporation of all volatile components was washed with *n*-hexane and dried under vacuum. Yield: 4.0 g (94%), mp > 350°C,  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 2.02 (s);  $^{19}\text{F}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 97.5 (m), -26.3 (m), -50.7 (m), -72.7 (m); EI-MS (70 eV): m/z 831 ( $\text{C}_{30}\text{H}_{45}\text{F}_8\text{Zr}_3$ , 100%).

— Elemental analysis:  $\text{C}_{10}\text{H}_{15}\text{F}_3\text{Zr}$  (283.45), Found: C 42.2, H 5.5, F 19.0; Reported: C 42.4, H 5.3, F 20.1.

### Example B

#### Pentamethylcyclopentadienylhafnium trifluoride

A mixture of 4.6 g (11.0 mmol) pentamethylcyclopentadienylhafnium trichloride and 6.0 g (32.9 mmol)  $[\text{Me}_3\text{SnF}]$  was combined with 80 mL toluene and was reacted and worked up as described in Example A. Yield: 3.7 g (93%), mp > 350°C,  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 2.07 (s);  $^{19}\text{F}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 41.8 (m), -54.0 (m), -77.3 (m), -97.8 (m); EI-MS (70 eV): m/z 1093 ( $\text{C}_{30}\text{H}_{45}\text{F}_8\text{Hf}_3$ , 40%).

— Elemental analysis:  $\text{C}_{10}\text{H}_{15}\text{F}_3\text{Hf}$  (370.71), Found: C 31.1, H 4.3, F 15.2; Reported: C 32.4, H 4.1, F 15.4.

### Example C

#### Bis(pentamethylcyclopentadienyl)zirconium difluoride

A mixture of 2.00 g (4.6 mmol) bis(pentamethylcyclopentadienyl)zirconium dichloride and 1.69 g (9.24 mmol) trimethylzinc fluoride was combined with 40 mL toluene and heated under reflux for 0.5 hr.

After cooling, all volatile components were removed under vacuum. The residue was subjected to vacuum for an additional hour at 80°C.

The remaining white solid was washed with a small amount of hexane and dried under vacuum. Bis(pentamethylcyclopentadienyl)zirconium difluoride was obtained in a yield of 89% (1.64 g). The melting point was 205°C.

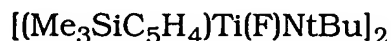
Mass spectrum:  $m/z = 398$  molecular peak with correct isotope distribution

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ , TMS external):  $\delta = 1.83$  ppm (triplet)

$^{19}\text{F-NMR}$  ( $\text{C}_6\text{D}_6$ ,  $\text{CFCl}_3$  external):  $\delta = +28.61$  ppm

IR spectrum: 1260, 1092, 1021; 800, 548, 535, 398, 376  $\text{cm}^{-1}$ ; correct elemental analysis

### Example D



A mixture of 1.02 g (2.75 mmol)  $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{Ti}(\text{Cl})\text{NtBu}$ -pyridine and 0.50 g (2.75 mmol)  $\text{Me}_3\text{SnF}$  was combined with 50 mL toluene and stirred at 90°C for 0.5 hr. The mixture was allowed to cool to room temperature and all volatile components were removed under vacuum. The remaining red solid was taken up in a small amount of hexane. After cooling to -20°C,  $[(\text{Me}_3\text{SiC}_5\text{H}_4)\text{Ti}(\text{F})\text{NtBu}]_2$  was obtained after 12 hr in the form of red crystals in a yield of 95% (0.72 g) and with a melting point of 218°C.

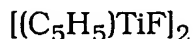
$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ , TMS external):  $\delta = 0.31$  (s, 9H,  $\text{Me}_3\text{Si}$ ), 1.05 (s, 9H, Bu), 5.95 (dd, 2H), 6.99 (dd, 2H) ppm

$^{19}\text{F-NMR}$  ( $\text{C}_6\text{D}_6$ ,  $\text{CFCl}_3$  external):  $\delta = 109.5$  ppm

Mass spectrum:  $m/z = 550$  dimer

IR spectrum: 840, 801, 623,  $595\text{ cm}^{-1}$

### Example E



A mixture of  $[(\text{C}_5\text{H}_5)\text{TiCl}]_2$  (0.64 g, 1.5 mmol) and  $\text{Me}_3\text{SnF}$  (0.55 g, 3 mmol) was combined with 60 mL toluene and stirred at room temperature. The solvent was removed under vacuum after all the  $\text{Me}_3\text{SnF}$  had gone into solution. The residue was crystallized from THF/hexane as green crystals.

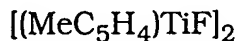
Yield: 0.53 g (90%), melting point:  $228^\circ\text{C}$

IR: 3091, 1093, 793, 471,  $380\text{ cm}^{-1}$

Mass spectrum:  $m/z = 197\text{ M}^+$

Correct elemental analysis

### Example F



The synthesis was analogous to that for  $[(\text{C}_5\text{H}_5)\text{TiF}]_2$ . Yield 92%, melting point  $94.5^\circ\text{C}$ , mass spectrum:  $m/z = 225\text{ M}^+$ .

### Example G



1.06 g (3 mmol)  $(\text{C}_5\text{Me}_5)_2\text{TiCl}$  was dissolved in 30 mL toluene and added dropwise to a suspension of 0.55 g (3 mmol)  $\text{Me}_3\text{SnF}$  in 30 mL toluene. The solid disappeared after stirring for three hours at room temperature. The solvent was then removed under vacuum and the residue was sublimed. 0.88 g (88%) of a green solid was obtained. Melting point:  $184^\circ\text{C}$ , mass spectrum:  $m/z = 337$ ,  $\text{M-Me}$ .

## Polymerization Examples

All glass instruments were heated in vacuo and flushed with argon. All operations were carried out with exclusion of moisture and oxygen in Schlenk flasks. The solvents used were freshly distilled over Na/K alloy under argon and kept in Schlenk flasks.

The aluminum determination was performed after hydrolysis by water and sulfuric acid by complexometric titration according to Schwarzenbach.

Toluene-soluble methylaluminoxane was used for the polymerization examples as the 10% toluene solution from Schering AG, which contained 36 mg Al/mL by aluminum determination. The average degree of oligomerization by freezing point depression in benzene was  $n = 20$ .

### Example 1

A dry 1.5 dm<sup>3</sup> stirred reactor was flushed with nitrogen to remove oxygen, filled with 0.9 dm<sup>3</sup> inert diesel oil (boiling point 100–120°C), and heated to 70°C. In parallel with this operation, 1.0 mg bis(pentamethylcyclopentadienyl)zirconium difluoride was dissolved in a 10 wt% solution of methylaluminoxane in toluene (12 mmol Al) and preactivated by stirring. The polymerization was initiated by injecting the catalyst solution and applying a pressure of 7 bar ethylene. After 1 hr at 70°C, the reactor was depressurized and the polymer was filtered from the suspension and dried for 12 hr in a vacuum drying oven. The result was 60.9 g polyethylene powder, corresponding to 3480 g-PE/mmol-Zr/hr/bar, having a viscosity number of 150 cm<sup>3</sup>/g. The molar mass distribution as determined by gel permeation chromatography was  $M_w/M_n = 2.6$ .

### Example 2

Example 1 was repeated using 11.0 mg pentamethylcyclopentadienylzirconium trifluoride. The result was 20 g polyethylene powder, corresponding to 70 g-PE/mmol-Zr/hr/bar, having a viscosity number of 600 cm<sup>3</sup>/g. The molar mass distribution as determined by gel permeation chromatography was  $M_w/M_n = 2.7$ .

### Comparative Example

The polymerization of Example 1 was repeated, except that 0.50 mg bis(pentamethylcyclopentadienyl)zirconium dichloride was used as catalyst. Under otherwise identical conditions, the result was 21 g polyethylene, corresponding to 2600 g-PE/mmol-Zr/hr/bar, having a viscosity number of 200 cm<sup>3</sup>/g. The molar mass distribution as determined by gel permeation chromatography was  $M_w/M_n = 2.6$ .

### Patent Claims

1. Method for producing  $\pi$ -system-containing organometallic fluorides with general formulas I, II, III, IV, V, and VI



wherein

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

the groups  $R^1$  are the same or different and represent hydrogen,  $C_1$  to  $C_{20}$  alkyl,  $C_6$  to  $C_{14}$  aryl,  $C_2$  to  $C_{10}$  alkenyl,  $C_7$  to  $C_{20}$  arylalkyl, or  $C_7$  to  $C_{15}$  alkylaryl, or  $SiR^3_3$  (wherein  $R^3$  is  $C_1$  to  $C_{10}$  alkyl), or neighboring  $R^1$  groups form one or several aliphatic or aromatic ring systems with the atoms that connect said  $R^1$  groups,

the groups  $R^5$  are the same or different and represent  $C_1$  to  $C_{10}$  alkyl,  $C_6$  to  $C_{10}$  aryl,  $C_1$  to  $C_{10}$  alkylaryl,  $NR^6_2$ ,  $OR^6$ ,  $SR^6$ ,  $OSiR^6_3$ ,  $>NR^6$ ,  $PR^6_2$ , or  $>PR^6$ , wherein each  $R^6$  is independently selected from hydrogen,  $C_1$  to  $C_{10}$  alkyl, and  $C_6$  to  $C_{10}$  aryl, and

$p = 1, 2$ , or  $3$ ,  $o = 0, 1$ , or  $2$ ,  $m = 4 - (p + o)$ ,  $n = 1, 2, 3, 4$ , or  $5$ ,  $(p + o) = 1, 2$ , or  $3$ ,  $q = 2$  when  $m = 1$ ,  $p = 1$ , and  $R^5 = >NR^6$  or  $>PR^6$ , and otherwise  $q = 1$ ;



wherein

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,



Cp is the cyclopentadienyl group,

the groups  $R^1$  are the same or different and represent hydrogen,  $C_1$  to  $C_{20}$  alkyl,  $C_6$  to  $C_{14}$  aryl,  $C_2$  to  $C_{10}$  alkenyl,  $C_7$  to  $C_{20}$  arylalkyl, or  $C_7$  to  $C_{15}$  alkylaryl, or  $SiR^3_3$  (wherein  $R^3$  is  $C_1$  to  $C_{10}$  alkyl), or neighboring  $R^1$  groups form one or several aliphatic or aromatic ring systems with the atoms that connect said  $R^1$  groups,

the groups  $R^2$  are the same or different and represent hydrogen,  $C_1$  to  $C_{20}$  alkyl,  $C_6$  to  $C_{14}$  aryl,  $C_2$  to  $C_{10}$  alkenyl,  $C_7$  to  $C_{20}$  arylalkyl, or  $C_7$  to  $C_{15}$  alkylaryl, or neighboring  $R^2$  groups form a ring system with the atoms that connect said  $R^2$  groups,

the groups  $R^5$  are the same or different and represent  $C_1$  to  $C_{10}$  alkyl,  $C_6$  to  $C_{10}$  aryl,  $C_1$  to  $C_{10}$  alkylaryl,  $NR^6_2$ ,  $OR^6$ ,  $SR^6$ ,  $OSiR^6_3$ ,  $>NR^6$ ,  $PR^6_2$ , or  $>PR^6$ , wherein each  $R^6$  is independently selected from hydrogen,  $C_1$  to  $C_{10}$  alkyl, and  $C_6$  to  $C_{10}$  aryl,

B is carbon or silicon, and

$k = 1, 2$ , or  $3$ ,  $p = 1$  or  $2$ ,  $o = 0$  or  $1$ ,  $n = 1, 2, 3, 4$ , or  $5$ ,  $(p + o) = 2$ ,  $q = 2$  when  $m = 1$ ,  $p = 1$ , and  $R^5 = >NR^6$  or  $>PR^6$ , and otherwise  $q = 1$ ;



wherein Cp,  $R^1$ ,  $R^2$ , M, B,  $k$ , and  $n$  are defined as in formula II,

said method **being characterized** by reacting a compound with general formula VII, VIII, IX, X, XI, or XII



wherein Cp,  $R^1$ ,  $R^5$ ,  $R^6$ , M,  $p$ ,  $o$ ,  $m$ ,  $n$ , and  $q$  are defined as in formula I and Y is chlorine, bromine, or iodine



wherein Cp, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, M, B, **k**, **p**, **o**, **n**, and **q** are defined as in formula II and Y is chlorine, bromine, or iodine



wherein Cp, R<sup>1</sup>, R<sup>2</sup>, B, Y, **k**, and **n** are defined as in formula II,

in an inert solvent with a tin fluoride with general formula XIII



wherein the groups R<sup>4</sup> are the same or different and represent C<sub>1</sub> to C<sub>10</sub> alkyl, C<sub>6</sub> to C<sub>14</sub> aryl, C<sub>2</sub> to C<sub>10</sub> alkenyl, C<sub>7</sub> to C<sub>20</sub> arylalkyl, or C<sub>7</sub> to C<sub>15</sub> alkylaryl.

2. Method according to Claim 1, characterized in that M in formulas I, II, III, IV, V, VI, VII, VIII, IX, X, XI, and XII represents titanium, zirconium, or hafnium.

3. Method according to Claim 1, characterized in that Y in formulas VII, VIII, IX, X, XI, and XII represents chlorine.

4. Method according to Claim 1, characterized in that R<sup>3</sup> in formula XIII represents C<sub>1</sub> to C<sub>10</sub> alkyl.

5. Use of a compound with formula XIII



to produce organometallic fluoride with general formula I, II, III, IV, V, or VI



wherein

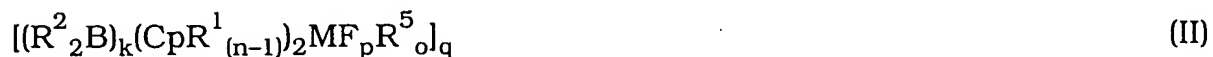
M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

the groups  $\text{R}^1$  are the same or different and represent hydrogen,  $\text{C}_1$  to  $\text{C}_{20}$  alkyl,  $\text{C}_6$  to  $\text{C}_{14}$  aryl,  $\text{C}_2$  to  $\text{C}_{10}$  alkenyl,  $\text{C}_7$  to  $\text{C}_{20}$  arylalkyl, or  $\text{C}_7$  to  $\text{C}_{15}$  alkylaryl, or  $\text{SiR}^3_3$  (wherein  $\text{R}^3$  is  $\text{C}_1$  to  $\text{C}_{10}$  alkyl), or neighboring  $\text{R}^1$  groups form one or several aliphatic or aromatic ring systems with the atoms that connect said  $\text{R}^1$  groups,

the groups  $\text{R}^5$  are the same or different and represent  $\text{C}_1$  to  $\text{C}_{10}$  alkyl,  $\text{C}_6$  to  $\text{C}_{10}$  aryl,  $\text{C}_1$  to  $\text{C}_{10}$  alkylaryl,  $\text{NR}^6_2$ ,  $\text{OR}^6$ ,  $\text{SR}^6$ ,  $\text{OSiR}^6_3$ ,  $>\text{NR}^6$ ,  $\text{PR}^6_2$ , or  $>\text{PR}^6$ , wherein each  $\text{R}^6$  is independently selected from hydrogen,  $\text{C}_1$  to  $\text{C}_{10}$  alkyl, and  $\text{C}_6$  to  $\text{C}_{10}$  aryl, and

$p = 1, 2$ , or  $3$ ,  $o = 0, 1$ , or  $2$ ,  $m = 4 - (p + o)$ ,  $n = 1, 2, 3, 4$ , or  $5$ ,  $(p + o) = 1, 2$ , or  $3$ ,  $q = 2$  when  $m = 1$ ,  $p = 1$ , and  $\text{R}^5 = >\text{NR}^6$  or  $>\text{PR}^6$ , and otherwise  $q = 1$ ;



wherein

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

the groups  $\text{R}^1$  are the same or different and represent hydrogen,  $\text{C}_1$  to  $\text{C}_{20}$  alkyl,  $\text{C}_6$  to  $\text{C}_{14}$  aryl,  $\text{C}_2$  to  $\text{C}_{10}$  alkenyl,  $\text{C}_7$  to  $\text{C}_{20}$  arylalkyl, or  $\text{C}_7$  to  $\text{C}_{15}$  alkylaryl, or  $\text{SiR}^3_3$  (wherein  $\text{R}^3$  is  $\text{C}_1$  to  $\text{C}_{10}$  alkyl), or neighboring  $\text{R}^1$  groups form one or several aliphatic or aromatic ring systems with the atoms that connect said  $\text{R}^1$  groups,

the groups  $\text{R}^2$  are the same or different and represent hydrogen,  $\text{C}_1$  to  $\text{C}_{20}$  alkyl,  $\text{C}_6$  to  $\text{C}_{14}$  aryl,  $\text{C}_2$  to  $\text{C}_{10}$  alkenyl,  $\text{C}_7$  to  $\text{C}_{20}$  arylalkyl, or  $\text{C}_7$  to  $\text{C}_{15}$  alkylaryl, or neighboring  $\text{R}^2$  groups form a ring system with the atoms that connect said  $\text{R}^2$  groups,

the groups  $\text{R}^5$  are the same or different and represent  $\text{C}_1$  to  $\text{C}_{10}$  alkyl,  $\text{C}_6$  to  $\text{C}_{10}$  aryl,  $\text{C}_1$  to  $\text{C}_{10}$  alkylaryl,  $\text{NR}^6_2$ ,  $\text{OR}^6$ ,  $\text{SR}^6$ ,  $\text{OSiR}^6_3$ ,  $>\text{NR}^6$ ,  $\text{PR}^6_2$ , or  $>\text{PR}^6$ , wherein each  $\text{R}^6$  is independently selected from hydrogen,  $\text{C}_1$  to  $\text{C}_{10}$  alkyl, and  $\text{C}_6$  to  $\text{C}_{10}$  aryl,

B is carbon or silicon, and

**k** = 1, 2, or 3, **p** = 1 or 2, **o** = 0 or 1, **n** = 1, 2, 3, 4, or 5, (**p** + **o**) = 2, **q** = 2 when **m** = 1, **p** = 1, and  $R^5 = >NR^6$  or  $>PR^6$ , and otherwise **q** = 1;



wherein Cp,  $R^1$ ,  $R^2$ , M, B, **k**, and **n** are defined as in formula II.

#### 6. Compound with formula I



in which

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

the groups  $R^1$  are the same or different and represent hydrogen,  $C_1$  to  $C_{20}$  alkyl,  $C_6$  to  $C_{14}$  aryl,  $C_2$  to  $C_{10}$  alkenyl,  $C_7$  to  $C_{20}$  arylalkyl, or  $C_7$  to  $C_{15}$  alkylaryl, or  $SiR^3_3$  (wherein  $R^3$  is  $C_1$  to  $C_{10}$  alkyl) or neighboring  $R^1$  groups form one or several aliphatic or aromatic ring systems with the atoms that join said  $R^1$  groups,

the groups  $R^5$  are the same or different and represent  $C_1$  to  $C_{10}$  alkyl,  $C_6$  to  $C_{10}$  aryl,  $C_1$  to  $C_{10}$  alkylaryl,  $NR^6_2$ ,  $OR^6$ ,  $SR^6$ ,  $OSiR^6_3$ ,  $NR^6$ ,  $PR^6_2$ , or  $PR^6$  (wherein the groups  $R^6$  are the same or different and represent hydrogen,  $C_1$  to  $C_{10}$  alkyl, or  $C_6$  to  $C_{10}$  aryl), and

**p** = 1 or 3, **o** = 0, 1, or 2, **m** = 4 - (**p** + **o**), **n** = 1, 2, 3, 4, or 5, (**p** + **o**) = 1, 2, or 3, **q** = 2 when **m** = 1, **p** = 1, and  $R^5 = >NR^6$  or  $>PR^6$ , and otherwise **q** = 1.

#### 7. Compound according to Claim 6, characterized in that M represents titanium, zirconium, or hafnium.

## 8. Compound with formula II



in which

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

the groups  $R^1$  are the same or different and represent hydrogen,  $C_1$  to  $C_{20}$  alkyl,  $C_6$  to  $C_{14}$  aryl,  $C_2$  to  $C_{10}$  alkenyl,  $C_7$  to  $C_{20}$  arylalkyl, or  $C_7$  to  $C_{15}$  alkylaryl, or  $SiR^3_3$  (wherein  $R^3$  is  $C_1$  to  $C_{10}$  alkyl), or neighboring  $R^1$  groups form one or several aliphatic or aromatic ring systems with the atoms that join said  $R^1$  groups,

the groups  $R^2$  are the same or different and represent hydrogen,  $C_1$  to  $C_{20}$  alkyl,  $C_6$  to  $C_{14}$  aryl,  $C_2$  to  $C_{10}$  alkenyl,  $C_7$  to  $C_{20}$  arylalkyl, or  $C_7$  to  $C_{15}$  alkylaryl, or neighboring  $R^2$  groups form a ring system with the atoms that join said  $R^2$  groups,

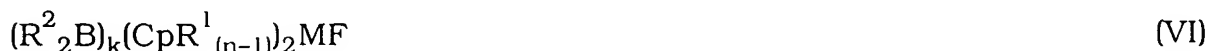
the groups  $R^5$  are the same or different and represent  $C_1$  to  $C_{10}$  alkyl,  $C_6$  to  $C_{10}$  aryl,  $C_1$  to  $C_{10}$  alkylaryl,  $NR^6_2$ ,  $OR^6$ ,  $SR^6$ ,  $OSiR^6_3$ ,  $>NR^6$ ,  $PR^6_2$ , or  $>PR^6$ , (wherein the groups  $R^6$  are the same or different and represent hydrogen,  $C_1$  to  $C_{10}$  alkyl, or  $C_6$  to  $C_{10}$  aryl),

B is carbon or silicon, and

$k = 1, 2$ , or  $3$ ,  $p = 1$  or  $2$ ,  $o = 0$  or  $1$ ,  $n = 1, 2, 3, 4$ , or  $5$ ,  $(p + o) = 2$ ,  $q = 2$  when  $m = 1$ ,  $p = 1$ , and  $R^5 = >NR^6$  or  $>PR^6$ , and otherwise  $q = 1$ .

9. Compound according to Claim 8, characterized in that M represents titanium, zirconium, or hafnium.

10. Compounds with formulas III, IV, V, and VI



in which

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

the groups  $R^1$  are the same or different and represent hydrogen,  $C_1$  to  $C_{20}$  alkyl,  $C_6$  to  $C_{14}$  aryl,  $C_2$  to  $C_{10}$  alkenyl,  $C_7$  to  $C_{20}$  arylalkyl, or  $C_7$  to  $C_{15}$  alkylaryl, or  $SiR^3_3$  (wherein  $R^3$  is  $C_1$  to  $C_{10}$  alkyl), or neighboring  $R^1$  groups form one or several aliphatic or aromatic ring systems with the atoms that join said  $R^1$  groups,

the groups  $R^2$  are the same or different and represent hydrogen,  $C_1$  to  $C_{20}$  alkyl,  $C_6$  to  $C_{14}$  aryl,  $C_2$  to  $C_{10}$  alkenyl,  $C_7$  to  $C_{20}$  arylalkyl, or  $C_7$  to  $C_{15}$  alkylaryl, or neighboring  $R^2$  groups form a ring system with the atoms that join said  $R^2$  groups,

B is carbon or silicon, and

$k = 1, 2, \text{ or } 3$  and  $n = 1, 2, 3, 4, \text{ or } 5$ .